

Synthesis and luminescent chemosensory behavior of N,N'-bis(p-aminophenyl)-1,5-bis(p-(tetraethyleneglycoloxy)phenyl)anthracene-2,3,6,7-tetracarboxyl bisimide

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Intermolecular interactions may be signaled by changes in photoinduced properties, such as absorption, emission intensity or wavelength, and luminescence lifetime.¹ Quenching of photoluminescence intensity is of particular interest as sensitivity is inherently enhanced due to a distinct contrast between signaling events (i.e. luminescent and nonluminescent states).¹ Researchers have utilized photoinduced electron transfer (PET), energy transfer, and others to produce “on/off” sensors based on aromatic and polycyclic aromatic hydrocarbons, aromatic heterocycles, and transition metal complexes.¹ Each approach targets specific sensing applications and maintains distinct advantages and disadvantages that warrant continued investigations.

Recently, chemical sensing of warfare agents has gained increasing attention.² Swager et al. reported an elegant example of functional group specific chemosensors that incorporated a transduction/cyclization process specific to highly reactive organophosphates and related compounds.^{2c} Our design of chemical sensors is based on creating new luminescent species that may be functionalized to respond to generic or specific target molecules.

Anthracene-based sensors encompass all areas of molecular recognition; for example, anion sensors^{1d,1e}, glucose sensors^{1d,3}, and metal-organic switches⁴. Anthracene is exploited due to its relative abundance (i.e. low cost) and depth of synthetic manipulation. Anthracene also possesses favorable photophysical properties, such as strong absorption and high quantum yield. Limitations include photoinduced cycloaddition reactions and formation of peroxides in the presence of oxygen.⁵ We report herein the synthesis and evaluation of the luminescent properties of two chromophores, **4** and **5**, based on a highly substituted anthracene bisimides.⁶ Figure 1 illustrates the potential of bisimide **5** (or ABI-NH₂, discussed later) in optical-based chemical sensing.

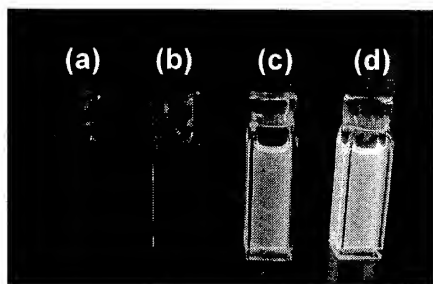


Figure 1. Luminescence (optically matched in DMF with excess analyte) of (a) **5**, (b) **5** with triethyl amine after addition of *p*-toluene sulfonic acid, (c) **5** with *p*-toluene sulfonic acid, and (d) **5** with thionyl chloride.

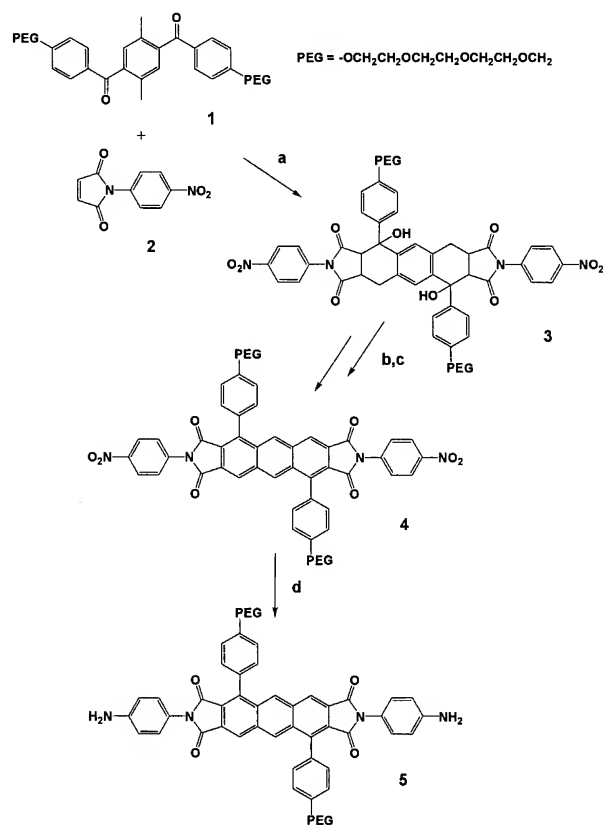


Figure 2. (a) *hν*, benzene (b) *p*-toluene sulfonic acid monohydrate, toluene (c) DDQ, chlorobenzene (d) 5% Pd/C, formic acid, DMF

We have recently developed a method for preparing substituted anthracenes based on the photoenolization of 2,5-dibenzoyl-*p*-xylene (DBX) derivatives.⁷ The photoenol of DBX is trapped *in situ* by a reactive dieneophile to produce the cycloadduct.⁷ Dehydration of this compound and subsequent aromatization yields highly substituted anthracene derivatives.^{6b-d} Following this methodology, 2,5-bis(*p*-(tetraethyleneglycoloxy)benzoyl)-*p*-xylene, **1**, was irradiated for 18 hours in the presence of two equivalents of *N*-(*p*-nitrophenyl) maleimide, **2**, to produce **3** in high yield (98%) as a mixture of stereoisomers. This is a synthetically mild step that has the potential to be used with a wide array of functional groups. Furthermore, addition of tetraethyleneglycoloxy (PEG) enhanced solubility in common organic media. Subsequent dehydration and aromatization of **3** produced N,N'-bis(*p*-nitrophenyl)-1,5-bis(*p*-(tetraethyleneglycoloxy)phenyl)anthracene-2,3,6,7-tetracarboxyl bisimide (**4** or ABI-NO₂) in moderate overall yield (34%). This sequence represents more rigorous experimental conditions and care must be taken to design a system that will maintain its chemical integrity.

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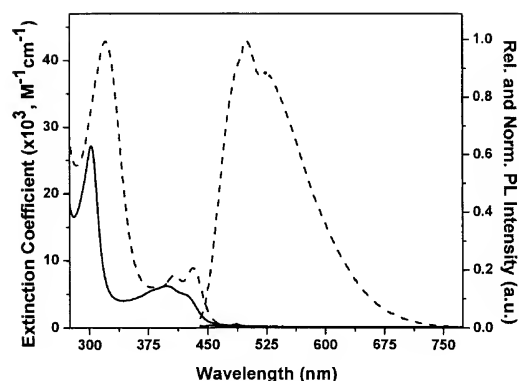


Figure 3. Absorption spectra (black lines) and relative, normalized emission spectra (blue lines) for **5** (solid lines) and **4** (dashed lines). Spectra were recorded in anhydrous DMF with 425 nm excitation.

Photophysical evaluation of ABI-NO₂ (DMF, $\sim 1 \times 10^{-5}$ M) revealed unique properties (i.e. not reminiscent of anthracene), Figure 3 exhibits this data. The absorption spectrum displayed two vibrational bands in the visible region ($\lambda_{\text{max}} = 408$ and 432 nm, $\epsilon = 7,800$ and $8,900 \text{ M}^{-1}\text{cm}^{-1}$, respectively). Steady-state fluorescence experiments revealed a broad, green emission ($\lambda_{\text{max}} = 499$ nm with a shoulder near 530 nm). Although the quantum yield of ABI-NO₂ in anhydrous DMF ($\Phi = 0.05$) was significantly less than that of anthracene in cyclohexane ($\Phi = 0.34$), the bisimide derivative demonstrated good photostability (<5% loss of signal intensity in 24 hours) when continuously irradiated at 425 nm (150 W Xe lamp, 8 mm slit width) in the presence of oxygen. The resistance of ABI-NO₂ to excited state reaction with oxygen is likely due to dramatic changes in electronic structure, which is supported by unique absorption and emission spectra. Further investigation of ABI-NO₂ showed no unexpected reactivity with traditional acids or acid halides.

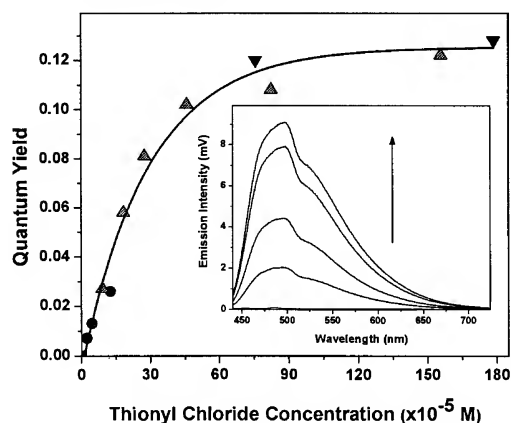


Figure 4. Luminescence titration curve in anhydrous DMF for **5** with additions of thionyl chloride. The complete curve represents three independent experiments with varying initial concentrations of thionyl chloride ($\bullet = 2 \times 10^{-5}$ M, $\blacktriangle = 9 \times 10^{-5}$ M, $\blacktriangledown = 75 \times 10^{-5}$ M). Inset: Selected emission spectra recorded with 425 nm excitation.

Reduction of ABI-NO₂ with formic acid and Pd/C gave the title compound, N,N'-bis(*p*-aminophenyl)-1,5-bis(*p*-(tetraethyleneglycoloxy)phenyl)anthracene-2,3,6,7-tetracarboxyl bisimide (**5** or ABI-NH₂), in high yield (88%).⁸ Initial inquiry into the properties of ABI-NH₂ showed an absorption spectrum similar to that of ABI-NO₂ (Figure 3). Unlike the nitro substituted compound, however, emission from ABI-NH₂ was nearly completely quenched. It is reasonable to suggest that quenching is due to intramolecular PET from the amine substituents.^{1,9} ABI-NH₂ also displayed similar stability toward reaction with oxygen

that was noted with ABI-NO₂. Continuous excitation with 425 nm light from a 150 W Xe lamp in the presence of oxygen resulted in minimal changes in absorption intensity and no fluorescence increase.

Reaction of ABI-NH₂ with organic acid halides, such as acetyl chloride, or with SOCl₂ gave rise to dramatic fluorescence enhancement. These acid halides mimic the behavior of organophosphonate-based nerve gasses and offer a safer alternative to evaluating the effectiveness of luminescent nerve gas sensors.^{2c} Figure 4 shows the luminescence titration curve for the reaction of ABI-NH₂ with SOCl₂. The response was converted to quantum yield for all data points due to the absence of a clear isospeic point. Conversion of the amines in ABI-NH₂ to the corresponding amides suppresses PET quenching pathway and the resulting products display luminescence properties similar to ABI-NO₂.⁹ Acids can also turn "on" the luminescence of ABI-NH₂ by reversible protonation of the pendant amines. It should be noted that prolonged exposure of ABI-NH₂ to acidic conditions, either directly from mixing with acid or indirectly from acid halide reaction products, resulted in loss of emission intensity. We are currently investigating this phenomenon.

In summary, we have utilized the photoenolization reaction of a dibenzoyl-*p*-xylene derivative to synthesize two new, highly substituted anthracene-based molecules. ABI-NO₂ and ABI-NH₂ maintained photostability with longer wavelength absorption and emission spectra as compared to unsubstituted anthracene. Conversion of the periphery nitro groups to amines created an internal photoinduced electron transfer scenario that quenched the luminescence of ABI-NH₂. Reversible or irreversible reaction of the attached amines resulted in fluorescence recovery. Sensitivity, of ABI-NH₂ and other potential derivatives, to toxic chemicals may prove useful for early detection systems.

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Supporting Information Available. Data and synthetic preparations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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